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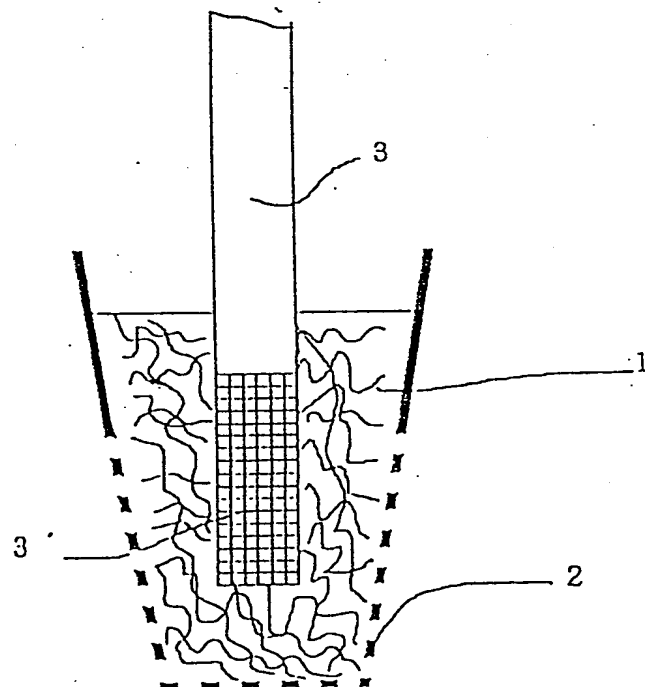
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(54) 【発明の名称】 油脂または油選択吸収体及びそれを用いた油水分離器

(57) 【要約】

【課題】 固体表面あるいは水と油のエマルジョンを含む廃水中の油脂または油分を短時間で、かつ充分に除去できる油選択吸収体及び油水分離器を提供する。

【解決手段】 超高分子量ポリオレフィンまたはそのポリオレフィン組成物からなる特定の空孔率及び貫通孔径を有するポリオレフィン微多孔膜からなる油脂または油選択吸収体、その積層体及びこれらを多孔性容器に充填した油水分離器。



## (特許請求の範囲)

【請求項1】 重量平均分子量が $5 \times 10^4$ 以上のポリオレフィンまたはその成分を含むポリオレフィン組成物からなり、空孔率が30～95%及び平均貫通孔径が0.001～1 $\mu$ mであるポリオレフィン微多孔膜からなる油脂または油選択吸収体。

【請求項2】 請求項1に記載の油選択吸収体において、前記ポリオレフィン微多孔膜が、フィルム状、短冊状、チップ状または塊状である油脂または油選択吸収体。

【請求項3】 請求項1または2に記載の油選択吸収体と、多孔性基材とを積層してなる油選択吸収体。

【請求項4】 請求項1～3のいずれかの項に記載の油選択吸収体を、多孔性容器に充填し、その充填物中に給水管を設けてなる油水分離器。

## (発明の詳細な説明)

(0001)

【発明の属する技術分野】 本発明は、超高分子量ポリオレフィンまたはその成分を含有するポリオレフィン微多孔膜からなる油脂または油選択吸収体、その積層体からなる油選択吸収体及びそれを用いた油水分離器に関し、特に固体表面の油脂または油類、廃水中の油類などを吸収する油脂または油選択吸収体及び油水分離器に関する。

(0002)

【従来の技術】 従来、固体表面または油類混合廃水から油脂や油分を分離除去するには各種の手段が用いられている。例えば、化粧直しの際の皮膚表面の油脂を取るには、紙製の「あぶら取り紙」が用いられているが、一回当りの吸着量は必ずしも十分でなく、そのためファンデーションを使用する必要があり、そのために「粉白粉付あぶら取り紙」まで市販されている。また、手などに付着した油あるいは金属などの固体表面に付着した油を拭き取るために種々の製品が市販されているが、これらの製品では拭うだけで短時間にかつ完全に除去するのは困難であった。

【0003】 一方、各種産業廃水、船舶のバラスト水、ガソリンスタンドの廃水などのように水中に分散した油分の除去処理には、凝集沈殿、酸分解法、膜分離法などと並んで吸着法が活用されている。この吸着法には、各種の有機、無機の多孔体、有機繊維質体などが使用されている。液体中の油分の分離方法として例えば、微細な油滴を含む液体を0.01～10 $\mu$ mの平均孔径を有する微多孔膜で処理することにより、油滴を濾別および／または凝集させる方法（特開昭51-131476号公報）、多孔体の内部及び表面を熱可塑性樹脂微孔シートで包囲して筒状にした分離要素を備えた分離装置（特開昭53-2390号公報）、油を含む水エマルジョンの被処理液を、膜表面の臨界面張力が35dyne/cm未満20dyne/cm以上で、平均孔径が0.03～5

$\mu$ m以下、孔径分布が1.5以下、エマルジョンの平均粒子径（ $\gamma E$ ）と上記平均孔径（ $\gamma$ ）との関係が $2\gamma E \geq \gamma$ ので、空孔率1～85%の貫通孔径の多孔膜表面に接触させ、油を選択的に透過分離させる方法（特開昭55-79011公報）などの開示がある。

【0004】 しかしながら、従来の液体中の油の選択的吸着または分離方法は、使用できてはいるもののその吸着速度などにおいては必ずしも充分ではなかった。さらに油吸着の程度を判別するのは容易ではなかった。

10 (0005)

【発明が解決しようとする課題】 本発明の課題は、固体表面あるいは水と油のエマルジョンを含む廃水中の油脂または油分を短時間でかつ充分に除去できる油脂または油選択吸収体及び油水分離器を提供することである。さらに油脂または油吸着の程度を目視で容易に判別できる油選択吸収体等の製品を提供することである。

(0006)

【課題を解決するための手段】 本発明者らは、上記課題を解決するために鋭意研究の結果、超高分子量ポリオレフィンまたはその成分を含む組成物からなる特定の微多孔膜及びその積層体が油脂または油選択吸収体として優れ、油分を吸収すると透明になり、またそれを多孔性の容器に充填したものは廃水中の油分の分離に優れた性能を発揮することを見出し、本発明に想到した。

【0007】 すなわち、本発明の第一の油脂または油選択吸収体は、重量平均分子量が $5 \times 10^4$ 以上のポリオレフィンまたはその成分を含むポリオレフィン組成物からなり、空孔率が30～95%及び平均貫通孔径が0.001～1 $\mu$ mであるポリオレフィン微多孔膜からなるものである。

【0008】 また、本発明の第二の油選択吸収体は、上記第一の油選択吸収体と、多孔性基材とを積層してなるものである。

【0009】 さらに、本発明の油水分離器は、上記第一または第二の油選択吸収体を、多孔性容器に充填し、その充填物中に給水管を設けてなるものである。

(0010)

【発明の実施の形態】 まず、本発明の第一の油脂または油選択吸収体を形成するポリオレフィン微多孔膜について説明する。このポリオレフィン微多孔膜は、空孔率が30～95%、好ましくは40～90%である。空孔率が30%未満で油脂や油分の吸収速度が遅く、また吸収量も少く好ましくない。一方、95%を超えると膜の機械的物性が不十分となり実用性に劣る。また、その平均貫通孔径は、0.001～1 $\mu$ m、好ましくは0.03～0.5 $\mu$ mである。孔径が0.001 $\mu$ m未満では油の吸収速度が遅く、一方1 $\mu$ mを超えると吸着保持が難しくなる。さらに、引張り破断強度が500kg/cm<sup>2</sup>以上のものが高強度で裂けにくいために好ましい。

【0011】上記本発明のポリオレフィン微多孔膜を形成するポリオレフィン、重量平均分子量が $5 \times 10^4$ 以上、好ましくは $1 \times 10^4 \sim 1.5 \times 10^5$ のものである。重量平均分子量が $5 \times 10^4$ 未満では、ポリオレフィン微多孔膜の製造時の延伸工程において最大延伸倍率が低く、前記の物性を有する目的のポリオレフィン微多孔膜が得られない。一方、上限は特に限定的ではないが $1.5 \times 10^5$ を超えるものは、ポリオレフィン微多孔膜の製造時の成形性に劣る。

【0012】また、本発明におけるポリオレフィン微多孔膜は、後述のポリオレフィン微多孔膜の製造の際のポリオレフィン溶液の高濃度化と得られる微多孔膜の多孔性と強度の向上を図るために、重量平均分子量 $5 \times 10^4$ 以上、好ましくは $1 \times 10^4 \sim 1.5 \times 10^5$ の超高分子量ポリオレフィンと重量平均分子量 $1 \times 10^4$ 以上 $5 \times 10^4$ 未満のポリオレフィンとの組成物を用いることができる。このポリオレフィン組成物中の超高分子量ポリオレフィンの含有量は、ポリオレフィン組成物全体を100重量%として1重量%以上が好ましく、より好ましくは10～70重量%である。

【0013】上記ポリオレフィンとしては、エチレン、プロピレン、1-ブテン、4-メチルペンテン1-、1-ヘキセンなどを重合した結晶性の単独重合体、2段重合体、または共重合体及びこれらのブレンド物などがあげられる。これらのうちでは、ポリプロピレン、ポリエチレンが好ましく、強度の観点からは特に高密度ポリエチレン及びこれらの組成物などが好ましい。また、風合いの観点からは低密度ポリエチレン、長鎖分岐ポリエチレンなどが好ましい。

【0014】本発明のポリオレフィン微多孔膜の好ましい製造方法は、前記ポリオレフィンまたはポリオレフィン組成物に、これらの良溶媒を供給しポリオレフィンまたはポリオレフィン組成物の溶液を調製して、この溶液を押出機のダイよりシート状に押し出した後、冷却してゲル状組成物を形成して、このゲル組成物を加熱延伸し、しかる後残存する溶媒を除去するものである。より具体的には、例えば特開平3-64334号公報に開示されているような次の方法が採用できる。

【0015】例えば、原料となるポリオレフィンまたはポリオレフィン組成物の溶液は、上述のポリオレフィンまたはポリオレフィン組成物を、溶媒に加熱溶解することにより調製する。この溶媒としては、ポリオレフィンまたはポリオレフィン組成物を十分に溶解できるものであれば特に限定されない。例えば、ノナン、デカン、ウンデカン、ドデカン、流動パラフィンなどの脂肪族または環式の炭化水素、あるいは沸点がこれらに対応する鉱油留分などがあげられるが、溶媒含有量が安定なゲル状成形物を得るためには流動パラフィンのような揮発性の溶媒が好ましい。加熱溶解は、ポリオレフィンまたはポリオレフィン組成物が完全に溶解する温度で強力に攪

拌または押出機で混練しながら行う。その温度は、例えば140～250℃の範囲が好ましい。また、ポリオレフィンまたはポリオレフィン組成物の溶液の濃度は、10～80重量%好ましくは10～50重量%である。濃度が10重量%未満では、使用する溶媒量が多く経済的でないばかりか、シート状に成形する際に、ダイス出口でスウェルやネックインが大きくシートの成形が困難となる。なお、加熱溶解にあたってはポリオレフィンまたはポリオレフィン組成物の酸化を防止するために酸化防止剤を添加するのが好ましい。

【0016】次に、このポリオレフィンまたはポリオレフィン組成物の加熱溶液を好ましくはダイスから押し出して成形する。ダイスは、通常長方形の口金形状をしたシートダイスが用いられるが2重円筒状のインフレーションダイスなども用いることができる。シートダイスを用いた場合のダイスギャップは通常0.1～5mmであり、押し出し成形温度は140～250℃である。この際押し出し速度は、通常20～30cm/分ないし2～3m/分である。

【0017】このようにしてダイスから押し出された溶液は、冷却することによりゲル状組織に成形される。冷却は少なくともゲル化温度以下までは50℃/分以上の速度で行うのが好ましい。一般に冷却速度が遅いと、得られるゲル状組成物の高次構造が粗くなり、それを形成する疑似細胞単位も大きなものとなるが、冷却速度が速いと、密な細胞単位となる。冷却速度が50℃/分未満では、結晶化度が上昇し、延伸に適したゲル状組成物となりにくい。冷却方法としては、冷風、冷却水、その他の冷却媒体に直接接触させる方法、冷媒で冷却したロールに接触させる方法などを用いることができる。なお、ダイスから押し出された溶液は、冷却前あるいは冷却中に好ましくは1～10、より好ましくは1～5の引き取り比で引取ってもよい。引き取り比が10以上になるとネックインが大きくなり、また延伸時に破断を起こしやすくなり好ましくない。

【0018】次に、このゲル状成形物に延伸を行う。延伸はゲル状成形物を加熱し、通常のテンター法、ロール法、インフレーション法、圧延法もしくはこれらの方法の組み合わせによって所定の倍率で行う。延伸は定幅一軸延伸でも二軸延伸でもよいが、二軸延伸が好ましい。また、二軸延伸の場合は、縦横同時延伸または逐次延伸のいずれでもよい。延伸温度は、ポリオレフィンまたはポリオレフィン組成物の融点+10℃以下、好ましくは結晶分散温度から結晶融点未満の範囲である。また延伸倍率は原反の厚さによって異なるが、定幅一軸延伸では2倍以上が好ましく、より好ましくは3～30倍である。二軸延伸では面倍率で10倍以上が好ましく、より好ましくは15～400倍である。面倍率が10倍未満では延伸が不十分で高弾性、高強度の微多孔膜が得られない。一方、面倍率が400倍を超えると、延伸操作な

どで制約が生じる。

【0019】得られた延伸成形物は、溶剤で洗浄し残留する溶媒を除去する。洗浄溶剤としては、ペンタン、ヘキサン、ヘプタンなどの炭化水素、塩化メチレン、四塩炭素などの塩素化炭化水素、三フッ化エタンなどのフッ化炭化水素、ジエチルエーテル、ジオキサンなどのエーテル類などの易揮発性のものを用いることができる。これらの溶剤はポリオレフィン組成物の溶解に用いた溶媒に応じて適宜選択し、単独もしくは混合して用いる。洗浄方法は、溶剤に侵漬し抽出する方法、溶剤をシャワー

【0020】上述のような洗浄は、延伸成形物中の残留溶媒が1重量%未満になるまで行う。その後洗浄溶剤を乾燥するが、洗浄溶剤の乾燥方法は加熱乾燥、風乾などの方法で行うことができる。乾燥した延伸成形物は、結晶分岐温度～融点の温度範囲で熱固定することが望ましい。

【0021】以上のようにして製造したポリオレフィン微多孔膜は、空孔率が30～95%で平均貫通孔径が0.001～1 $\mu$ mで、かつ引張り破断強度が500kg/cm<sup>2</sup>以上である。また、ポリオレフィン微多孔膜の厚さは、その用途により選択されるが一般的には5～50 $\mu$ m程度である。

【0022】このようにして得られたポリオレフィン微多孔膜は、フィルム状、短冊状に裁断したもの、チップ状に裁断したもの、あるいは機械的または熱的に接加工を施したものなどの形状で油脂または油選択吸収体として使用できる。本発明の油選択吸収体に用いられるポリオレフィン微多孔膜は油脂または油を吸収すると透明になるので、油分吸収の程度を目視により容易に判断することができる。また、洗浄による繰返し使用が可能であることから種々の分野で使用することができる。

【0023】次に、本発明の第二の油選択吸収体について説明する。本発明の第二の油選択吸収体は、前記第一の油選択吸収体を形成するポリオレフィン微多孔膜と多孔性基材とを積層したものである。

【0024】上記多孔性基材としては、ポリオレフィン微多孔膜と積層できるものであれば任意の熱可塑性樹脂製の織布、不織布、多孔性膜、多孔性シート、または多孔性フィルムなどがあげられる。これらの中では前記ポリオレフィン微多孔膜との積層性のうからポリオレフィン製の不織布、例えば繊維直径が0.5～50 $\mu$ mのポリプロピレン製不織布が好ましい。

【0025】ポリオレフィン微多孔膜と多孔性基材との積層は、両方の空孔率を実質的に損なわないようにすることが必要である。好ましい積層加工方法としては、カレンダー加工、エンボス加工などがあげられるが、その他周囲の融着や間欠的な融着をする方法であってもよい。この積層により、油類の吸着保持性を高めるとも

に使用における実用性も高めることができる。

【0026】次に、本発明の油水分離器について説明する。本発明の油水分離器は、前記第一または第二の油選択吸収体を多孔性容器に充填し、その充填物中に給水管を設けたものである。

【0027】上記多孔性容器としては、前記油選択吸収体を充填できるものであれば、その材質や形状は特に限定されない。例えば、天然繊維または合成繊維からなる織布や不織布からなる袋状物、合成樹脂製の網または多孔板からなる容器、金属製の網または多孔板からなる容器などがあげられる。また、給水管は、油選択吸収体に挿入した部分が網または多孔となっているものがあげられる。

【0028】この油水分離器を実施例の図面を参照しつつ詳細に説明する。油水分離器は、図1に示されるように油選択吸収体1が、多孔性容器2、例えばステンレス製網状円筒容器2にほぼ上部まで充填され、その油選択吸収体1の中央部に給水管3、例えばステンレス製の挿入部が網状の管3が挿入されている。油分と水との混合廃水は、上記給水管3から供給され、多孔部分から充填された油選択吸収体1中に流出し、油分は油選択吸収体1に吸着されて浄化水が多孔性容器2の孔から流出する。

【0029】

【実施例】本発明について実施例をあげてさらに詳細に説明するが、本発明は実施例等に特に限定されるものではない。なお、試料は次のものを用いた。

(1) 試料1 (S-1) : 重量平均分子量が2.5 $\times 10^4$ の超高分子量ポリエチレン5.5重量部と重量平均分子量が3.5 $\times 10^4$ の高密度ポリエチレン24.5重量部のポリエチレン組成物100重量部に酸化防止剤0.375重量部を加えたポリエチレン組成物を得た。このポリエチレン組成物30重量部を二軸押出機(58mm $\phi$ 、L/D=42、強混練タイプ)に投入した。またこの二軸押出機のサイドフィダーから流動パラフィン70重量部を供給し、溶融混練して、押出機中にてポリエチレン溶液を調製した。

【0030】続いて、この押出機の先端に設置されたTダイから190 $^{\circ}$ Cで押し出し、冷却ロールで引取りながらゲル状シートを成形した。続いてこのゲル状シートを、115 $^{\circ}$ Cで5 $\times$ 5に同時2軸延伸を行い、延伸膜を得た。得られた延伸膜を塩化メチレンで洗浄して残留する流動パラフィンを抽出除去した後、乾燥および熱処理を行い、空孔率40%、平均貫通孔径0.03 $\mu$ m、厚さ25 $\mu$ mのポリエチレン微多孔膜を得た。

(2) 試料2 (S-2) : 上記ポリエチレン微多孔膜を幅2mmの短冊状に裁断したものを。

(3) 試料3 (S-3) : 前記S-1に熱機械的に接加工を施したものを。

(4) 試料4 (S-4) : 前記S-1を目付50g/m<sup>2</sup>

のポリプロピレン不織布2枚で挟み四辺を熱融着したもの。

(5) 試料5 (S-5) : 前記S-2を目付50g/m<sup>2</sup>

のポリプロピレン不織布2枚で挟み四辺を熱融着したもの。

(6) 試料6 (S-6) : 市販品の「あぶら取り紙」。

(7) 試料7 (S-7) : 市販品のバルブ製「ペーパータオル」。

(8) 試料8 (S-8) : 目付22g/m<sup>2</sup>のポリプロピレン不織布。

(9) 試料9 (S-9) : 前記S-6を幅2mmの短冊

状に裁断したもの。

(10) 試料10 (S-10) : 前記S-7を幅2mmの短冊状に裁断したもの。

(11) 試料11 (S-11) : 前記S-8を幅2mmの短冊状に裁断したもの。

【0031】実施例1~5、比較例1~3

ガラス平板上に粘度45cpsのバラフィンオイル1mlをスポイトで滴下し、その上に前記の試料1~8を乗せ軽く抑え、オイルの吸収性を評価した。結果を表1に示す。

【0032】

表1

	実施例1	実施例2	実施例3	実施例4	実施例5
試料	S-1	S-2	S-3	S-4	S-5
吸収性 <sup>iii</sup>	◎	◎	◎	○	○
	比較例1	比較例2	比較例3		
試料	S-6	S-7	S-8		
吸収性 <sup>iii</sup>	×	×	×		

吸収性<sup>iii</sup> : ◎は、オイルを瞬時に吸収して透明となり、ガラス平板上および試料表面上にオイル残留が認められず、試料中に吸着されたもの。○は、ガラス平板上のオイル残留は認められず、試料表面にオイル残留が僅かに認められるもの。×は、ガラス平板上にオイル残留が認められ、試料表面にも多量のオイルの付着が認められるもの。

【0033】実施例6~8、比較例4~6

水と前記バラフィンオイルを等量ホモジナイザーで微細な分散状態とし、この1mlをガラス平板上に滴下し、その上に試料1~3及び6~8を乗せ軽く抑え、オイルの吸収性を評価した。結果を表2に示す。

【0034】

表2

	実施例6	実施例7	実施例8	比較例4	比較例5	比較例6
試料	S-1	S-2	S-3	S-6	S-7	S-8
吸収性 <sup>iii</sup>	◎	◎	◎	×	×	×

吸収性<sup>iii</sup> : ◎は、試料が瞬時に透明となり、試料の表面及びガラス平板上に水が微細な滴状に認められ、オイルが選択的に吸着されたもの。×は、試料の表面及びガラス平板上に水とオイルの分散物が認められ、オイルの選択的吸着のないもの。

【0035】実施例9、比較例7~9

試料2及び9~11を、それぞれ10g図1に示すよう

なステンレス製網状円筒容器に詰め込み、その中央に挿入部分が網状のステンレス管を挿入し、管の上端から水90g/前記オイル10gの分散物100gを注ぎ込み、前記ステンレス製網状円筒容器からしみ出てくる液体を集め、エバポレーターで水を蒸発除去し、残留物の量を計測した。結果を表3に示す。

【0036】

表3

	実施例9	比較例7	比較例8	比較例9
試料	S-2	S-9	S-10	S-11
残留物	10mg <sup>iv</sup>	5.4g	3.7g	1.2g

なお、試験後の各試料(S-2)を多量のヘキサンで洗浄後に乾燥し、それぞれについて繰り返し試験を行ったが同様の結果が得られた。

【0037】以上、表1及び表2から明らかなように、本発明の油選択吸収体は、瞬時に油を吸収して多量に保持し、かつ油/水の混合物から油分を選択的に吸収する。また、本発明の油水分離器は、表3で示すように油/水の混合物から油分をほぼ完全に除去できることがわかる。

【0038】

【発明の効果】以上詳述したように、本発明の油選択吸収体は、固体表面の油脂や油分、または油/水の混合物中の油分を、短時間で多量に、かつ選択的に吸収保持できる。また、油水分離器は、油/水の混合物から油分を効率的に分離除去できる。したがって、各種分野で用いることができるが、油選択吸収体は、あぶら取り紙、油拭拭材などに有用である。また、油水分離器は、油分混合廃水の浄水化に有用である。

【図面の簡単な説明】

50 【図1】本発明の油水分離器の実施例を示した一部破断

KOKAI PATENT APPLICATION NO. HEI 10-15304

**SELECTIVE FAT AND OIL OR OILY SUBSTANCE ABSORBER  
AND/OR OIL SEPARATOR USING IT**

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[Translator's note: the above is handwritten in English]

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SELECTIVE FAT AND OIL OR OILY SUBSTANCE ABSORBER  
AND/OR OIL SEPARATOR USING IT

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*[There are no amendments to this patent.]*

*[Translator's note: Names of products and companies are spelled phonetically in this translation.]*



[Origin of the underlining that appears in the source document is not known to the translator.]

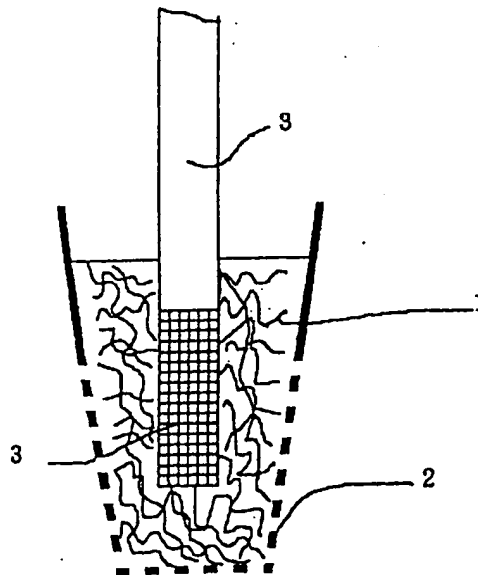
(54) [Title of the Invention]

Selective fat and oil or oily substance absorber and/or oil separator using it

(57) [Abstract]

[Purpose] The purpose of the present invention is to produce a selective fat and oil and/or an oily substance separator capable of removing fats and oils or oily substances on a solid surface or from a waste solution containing them as an emulsion of water and the oily substance, thoroughly, in a short time.

[Means of solution] A selective fat and oil or oily substance absorber comprising a super-high molecular weight polyolefin or a polyolefin composition made thereof and comprising a microporous polyolefin film having a specific porosity and pore diameter, and laminates thereof, or an oil separator comprising a porous container filled with said absorber.



[Claims of the invention]

[Claim 1] A selective fat and oil or oily substance absorber comprising a polyolefin having a weight average molecular weight of at least  $5 \times 10^4$  or a polyolefin composition containing the aforementioned component and having a structure comprising a microporous polyolefin film having a porosity in the range of 30 to 95% and a mean through-pore diameter of 0.001 to 1  $\mu\text{m}$ .

[Claim 2] The selective fat and oil or oily substance absorber described in Claim 1 in which the aforementioned microporous polyolefin film is in the form of a film, strips, chips, or crimped state.

[Claim 3] A selective oil absorber produced by laminating the selective fat and oil or oily substance absorber described in Claim 1 or Claim 2 and a porous substrate.

[Claim 4] An oil separator in which the selective fat and oil or oily substance absorber described in one of Claims 1 through 3 is used to fill a porous container and a feed line is installed within the filler.

**[Detailed description of the invention]**

[0001]

[Technical field of the invention] The present invention pertains to a selective fat and oil or oily substance absorber comprising a super-high molecular weight polyolefin or a microporous polyolefin film containing the component, a selective oil absorber made as a laminate, and an oil separator made thereof, and the invention further pertains to a selective fat and oil or oily substance absorber that absorbs fats and oils and oily components on a solid surface or oily components in waste water.

[0002]

[Prior art] In the past, a variety of methods have been used for separation of fats and oils or oily components from solid surfaces and waste water mixed with oils. For example, an "oil removal sheet" made of paper is used for removal of oily substances from the skin at the time of re-application of make-up, but the absorption per application is not necessarily sufficient, and a foundation is required, thus, "oil removal sheet with facial powder applied" is marketed as well. Furthermore, in order to remove oil absorbed on the hands, or oils adsorbed on a solid surface such as a metal surface, a variety of products are commercially available, but complete removal of the oil in a short time just by wiping is not possible when those products are used.

[0003] Moreover, for the removal of oily components dispersed in water such as in the waste water of many industries, ballast water of marine vessels, and waste water from gas stations, the adsorption method is used in combination with a sedimentation process, acid decomposition process, film separation process, etc. And a variety of organic or inorganic porous materials, organic fibrous materials, etc. are used in the above-mentioned absorption methods. As a method of separation used for oily components from a liquid, for example, a method in which a treatment is carried out for the liquid containing fine oil droplets using a microporous film having a mean pore diameter in the range of 0.01 to 10  $\mu\text{m}$  and filtration and/or coagulation of the oil droplets is applied (Japanese Kokai [Unexamined] Patent Application No. Sho 51-131476), separator equipped with a cylindrical separator in which the interior surface of a porous material is covered with a porous thermoplastic resin sheet (Japanese Kokai [Unexamined] Patent Application No. Sho 53-2390), a method in which selective separation of oily substances is carried out as an aqueous emulsion containing oil is brought into contact with the surface of a

porous film having a critical surface tension of the film surface in the range of 20 dyn/cm and 35 dyn/cm, mean pore diameter in the range of 0.05 to 5  $\mu$ m, a pore distribution of 1.5 or below, and having the relationship between the mean particle diameter of the emulsion ( $\gamma$  E) and the mean particle diameter of the solution ( $\gamma$ ) of  $2 \gamma$  E  $>$   $\gamma$ , and porosity in the range of 1 to 85% (Japanese Kokai [Unexamined] Patent Application No. Sho 55-79011), etc. are disclosed.

[0004] However, selective absorption and the separation methods for the solution used in the past have not necessarily been adequate from the standpoint of absorption rate, etc. And furthermore, the degree of oil absorption is difficult to judge.

[0005]

[Problems to be solved by the invention] The purpose of the present invention is to produce a selective fat and oil absorber and an oil separator capable of removing fats and oils or oily substances on a solid surface or in a waste solution containing an emulsion of water and an oily substance, thoroughly, in a short time. Furthermore, the purpose of the present invention is to produce a product such as a selective oil absorber in which the degree of absorption of fats and oils or oil separation can be easily judged visually.

[0006]

[Means to solve the problem] As a result of much research carried out by present inventors in an effort to achieve the above-mentioned purpose, they discovered that a specific microporous film made of a polyolefin with a super-high molecular weight or a composition containing said component, or a laminate thereof exhibits excellent selective fat and oil absorption or oil absorption, and becomes transparent upon absorption of oily components, and that when the above-mentioned absorber is used to fill a container, it can be used effectively for separation of

oil components in waste water, and the present invention was accomplished.

[0007] Thus, the first invention is a selective fat and oil absorber or an oil absorber comprising a polyolefin having a weight average molecular weight of at least  $5 \times 10^4$  or a polyolefin composition containing the aforementioned component and is structured of a microporous polyolefin film having porosity in the range of 30-95% and a mean through-pore diameter of 0.001-1  $\mu\text{m}$ .

[0008] Also, the second invention is a selective oil absorber produced by laminating the above-mentioned and a porous substrate.

[0009] Furthermore, in the oil separator of the present invention, the above-mentioned selective oil absorber is filled in a porous container and a feed line is installed among the filler.

[0010]

[Embodiment of the invention] First, the microporous polyolefin film that structures the selective fats and oils, or oil absorber of the present invention is explained below. The porosity of the aforementioned microporous polyolefin film is in the range of 30-95%, preferably, in the range of 40-90%. When the porosity is 30% or below, the absorption rate of the fats and oils or oil content is inadequate, and the amount absorbed is low. On the other hand, when the porosity exceeds 95%, the mechanical properties of the film become inadequate, and practical application is not possible. Furthermore, the mean diameter of the through-pore is in the range of 0.001-1  $\mu\text{m}$ , preferably, in the range of 0.03-0.5  $\mu\text{m}$ . When the pore diameter is 0.001  $\mu\text{m}$  or below, the absorption rate of oil is inadequate, and on the other hand, when the diameter exceeds 1  $\mu\text{m}$ , retention of absorbed state is made difficult. Furthermore, it is desirable for the tensile rupture strength of at least 500 kg/cm<sup>2</sup> from the standpoint of high strength and high tear resistance.

[0011] The weight average molecular weight of the polyolefin that structures the above-mentioned microporous polyolefin film of the present invention is at least  $5 \times 10^4$ , preferably, in the range of  $1 \times 10^4$  to  $15 \times 10^4$ . When the weight average molecular weight is  $5 \times 10^4$  or below, the maximum stretching ratio of the microporous polyolefin film is low at the time of production of the microporous polyolefin film, and the target microporous polyolefin film having the above-mentioned properties cannot be produced. On the other hand, the upper limit is not especially limited, but when the value exceeds  $15 \times 10^4$ , film formability of the microporous polyolefin film is not adequate.

[0012] Furthermore, in order to increase the concentration of the polyolefin solution at the time of production of the microporous polyolefin film described below, and to increase the porosity and strength of the microporous film produced, it is possible to use a composition comprising a super-high molecular weight polyolefin with a weight average molecular weight of at least  $5 \times 10^4$ , preferably, in the range of  $1 \times 10^4$  to  $15 \times 10^4$ , and a polyolefin with a weight average molecular weight in the range of  $1 \times 10^4$  to  $5 \times 10^4$  in the present invention. The amount of the super-high molecular weight polyolefin included in the above-mentioned polyolefin composition is at least 1 wt% for 100 wt% of the overall polyolefin composition and in the range of 10 to 70 wt% is especially desirable.

[0013] For the above-mentioned polyolefin, crystalline homopolymers where ethylene, propylene, 1-butene, 4-methyl-pentene-1, 1-hexene, etc. are polymerized, two-stage polymers, copolymers, blend polymers, etc. can be mentioned. In particular, polypropylene and polyethylene are desirable, and from the standpoint of strength, high-density polyethylene and compositions made thereof are further desirable. Furthermore, low-den polyethylene, long-chain

branched polyethylene, etc. are desirable from the standpoint of surface appearance.

[0014] In a suitable manufacturing method of the microporous polyolefin film of the present invention, a method in which the above-mentioned good solvent is supplied to the aforementioned polyolefin or polyolefin composition, extrusion is carried out for the solution from the die of the extruder to form a sheet, cooled to form a gel-like composition, stretching is performed for the aforementioned gel-like composition under heat, and removal of the solvent left behind is performed can be mentioned. In specific terms, the method described below and is disclosed in patent publication such as Japanese Kokai [Unexamined] Patent Application No. Hei 3-64334 can be used.

[0015] For example, the raw material polyolefin or polyolefin composition solution is produced by dissolving the above-mentioned polyolefin or polyolefin composition in a solvent. The solvent used in this case is not especially limited as long as the solvent is capable of adequately dissolving the polyolefin or polyolefin composition. For example, aliphatic or cyclic hydrocarbons such as nonane, decane, undecane, dodecane, and liquid paraffin, or mineral oil cut having a boiling point corresponding to the above-mentioned solvent can be mentioned, and in order to produce a gel-like material with a stable solvent content, a nonvolatile solvent such as liquid paraffin, is desirable. Dissolving under heat is done at a temperature sufficient to completely dissolve the polyolefin or polyolefin composition under vigorous stirring or mixing inside the extruder. It is desirable for the above-mentioned temperature to be in the range of 140 to 250°C. Furthermore, the concentration of the solution of the polyolefin or polyolefin composition is in the range of 10 to 80 wt%, preferably, in the range of 10 to 50 wt%. In the case when the concentration is 10 wt% or below, the amount of the solvent used is high and is not

economical, and swelling or neck-in at the exit of the die is significant when formed into a sheet, and sheet formation is made difficult. Furthermore, in order to prevent oxidation of the polyolefin or polyolefin composition at the time of dissolving under heat, it is desirable when an antioxidant is added.

[0016] Subsequently, the molten solution of the above-mentioned polyolefin or polyolefin composition is extruded from the die and molding is performed. In general, a sheet die having an die orifice with a rectangular shape is used, and a cylindrical inflation die may be used as well. In general, the die gap when the sheet die is used is in the range of 0.1 to 5 mm, and the extrusion molding temperature is in the range of 140 to 250°C. in general, the extrusion rate is in the range of 20 to 30 cm/min to 2 to 3 m/min.

[0017] The solution extruded from the die as described above is formed into a gel-like structure when cooling is performed. It is desirable when cooling is performed at a rate of 50°C/min up to at least a temperature of below gelation. In general, the high-order structure of the gel-like composition becomes rough when cooling rate is low and the analogue cell structure is increased, and when the cooling rate is high, the cell unit is concentrated. When the cooling rate is 50°C/min or below, crystallization temperature is increased and a composition suitable for stretching is less likely to be produced. For the cooling method, a method in which cooling of the composition is carried out directly with cooling medium such as chilled air or cold water, a method in which the composition is brought into contact with a chilled roll, etc. can be mentioned. Also, the solution extruded from the die may be taken-up before chilling or during the course of chilling at a take-up rate in the range of 1 to 10, preferably, in the range of 1 to 5. When the take-up rate exceeds 10, an increase in neck-in occurs; furthermore, rupturing is likely



to occur at the time of stretching.

[0018] Subsequently, stretching is carried out for the above-mentioned gel-like molded article.

Stretching is performed by heating the gel-like molded article and using a conventional method such as a standard tentering method, roll method, inflation method, rolling method, or a combination of these methods at a specific stretching ratio. Stretching may be done using uniaxial stretching or biaxial stretching, but biaxial stretching is preferable in this case.

Furthermore, when biaxial stretching is used, simultaneous stretching or successive stretching can be applied. The stretching temperature used is in the range of the melting point of the polyolefin or polyolefin composition +10°C, preferably, the crystal dispersion temperature to the crystal melting point. The stretching ratio varies depending on the thickness of the original sheet, and at least two times is desirable when constant-width uniaxial stretching is used, and in the range of 3 to 30 times is especially desirable. In the case of biaxial stretching, at least 10 times in terms of the area stretching ratio is desirable, and in the range of 15 to 400 times is especially desirable. When the area stretching ratio is less than 10, stretching is not sufficient, and a microporous film with a high modulus and high strength cannot be produced. On the other hand, when the area stretching ratio exceeds 400 times, stretching conditions, etc. are restricted.

[0019] The stretched molded article produced is cleaned with a solvent and residual solvent is removed. For the cleaning solvent used in this case, hydrocarbons such as pentane, hexane, and heptane, chlorinated hydrocarbons such as methylene chloride and carbon tetrachloride, fluorocarbons such as trifluoroethane, ethers such as diethyl ether and dioxane can be used. The above-mentioned solvents are appropriately selected according to the solvent used for dissolving of the polyolefin composition and used independently or in combination. As for the cleaning

method used, a method in which dipping is performed in the solvent and extraction is performed, washing of the solvent using shower, or a combination of these can be mentioned.

[0020] The above-mentioned cleaning is done until the residual solvent included in the stretched molded article is 1 wt% or less. Subsequently, the cleaning solvent is evaporated, and a drying method such as hot-air drying or air drying can be used in this case. It is desirable when a heat set is applied to the stretched molded article after drying at a temperature in the range of the crystal dispersion temperature to the melting point temperature.

[0021] The porosity of the microporous polyolefin film produced as described above is in the range of 30 to 95%, and the mean pore diameter is in the range of 0.001 to 1  $\mu\text{m}$ , and furthermore, the tensile rupture strength is at least 500 kg/cm<sup>2</sup>. Furthermore, the thickness of the microporous polyolefin film varies depending on the intended application, but, in general, the thickness is in the range of 5 to 50  $\mu\text{m}$ .

[0022] The microporous polyolefin film produced as described above is used in the form of a film, strips, chips, or a mechanically or thermally crimped form for the selective fat and oil absorber or oily substance absorber. The microporous polyolefin film used for the selective oil absorber of the present invention becomes transparent upon absorption of fats and oils or an oily substance; thus, the degree of oil absorption can be easily judged visually. Furthermore, reuse is possible upon washing; thus, the absorber can be used in a variety of fields.

[0023] Furthermore, a second selective oil absorber is explained below. The second selective oil absorber of the present invention is produced by laminating the aforementioned microporous polyolefin film that comprises the first selective oil absorber and a porous substrate.

[0024] The above-mentioned porous substrate is not especially limited as long as lamination with

a microporous polyolefin film is possible, and a woven cloth, non-woven fabric, porous film, porous film of a given thermoplastic resin can be mentioned. Among those listed above, a non-woven fabric made of polyolefin, for example, a polypropylene non-woven fabric having a fiber diameter in the range of 0.5 to 50  $\mu\text{m}$ , is especially desirable from the standpoint of ease of lamination with the aforementioned microporous polyolefin film.

[0025] It is important to prevent a reduction in porosity of both films upon lamination of the microporous polyolefin film and porous substrate. As suitable lamination methods, calendar fabrication, embossing, etc. can be mentioned, and furthermore, fusion can be done at edges as well. When lamination is done, absorption and retention of oils can be increased and the application range can be increased, as well.

[0026] In the following, the oil separator of the present invention is explained. The oil separator of the present invention is produced by placing the aforementioned first or second selective oil absorber in a porous container and installing a feed line in the filler.

[0027] For the above-mentioned porous container, the material and the shape used is not especially limited as long as the aforementioned selective oil absorber can be included. For example, a pack made of a woven cloth or non-woven fabric made of natural or synthetic fibers, a mesh made of a synthetic resin, a container made of a porous sheet, metal screen, or container made of a porous sheet can be mentioned. Furthermore, for the feed line, a line with the portion inserted into the selective oil absorber comprising a screen or a porous material is used.

[0028] The above-mentioned oil separator is further explained in detail with reference to the drawing. As shown in the oil separator of Fig. 1, selective oil absorber 1 is used to fill to fill porous container 2 nearly to the top; and, for example, a cylindrical stainless steel screen

container, feed line 3, for example, a line in which the inserted portion is made of stainless steel, is inserted into the center region of the selective oil absorber. The waste water containing the oily components and water is supplied through the above-mentioned feed line 3, the solution enters from the porous area to the selective oil absorber, the oily components are absorbed by the selective oil absorber and the purified water comes out of the openings in porous container 2.

[0029]

[Application Examples] The present invention is explained in further detail with application examples below, but the present invention is not limited to these application examples.

Furthermore, samples used are described below.

(1) Sample 1 (S-1): 0.375 parts by weight of antioxidant was added to 100 parts by weight of a polyethylene composition comprising 5.5 parts by weight of super high molecular weight polyethylene having a weight average molecular weight of  $2.5 \times 10^1$  and 24.5 parts by weight of a high-density polyethylene with a weight average molecular weight of  $3.5 \times 10^1$  to produce a polyethylene composition. 30 parts by weight of the above-mentioned polyethylene composition was poured into a biaxial extruder (diameter of 58 mm, L/D=42, forced-kneading type).

Furthermore, 70 parts by weight of liquid paraffin was fed from the side feed of the aforementioned biaxial extruder, and hot-melt mixing was carried out to produce a polyethylene solution inside the extruder.

[0030] Furthermore, extrusion was done from a T-die arranged on the tip of the aforementioned extruder at a temperature of 190°C, take-up was done with a chilled roll and production of a gel-like sheet was achieved. Subsequently, simultaneous biaxial stretching was applied to the gel-like sheet produced above at a temperature of 115°C to achieve a 5x5 stretch in the resulting

stretched film. Cleaning of the stretched film produced above was done with methylene chloride and residual liquid paraffin was removed, and the film dried; then, a heat-treatment was applied to produce a microporous polyethylene film with a porosity of 40%, mean through pore diameter of 0.03  $\mu\text{m}$  and a thickness of 25  $\mu\text{m}$ .

(2) Sample 2 (S-2): Aforementioned microporous polyethylene film cut to form strips with a width of 2 mm.

(3) Sample 3 (S-3): Aforementioned S-1 subjected to mechanical crimping under heat.

(4) Sample 4 (S-4): Aforementioned S-1 was placed between two pieces of polypropylene non-woven fabric with a metsuke of 50  $\text{g/m}^2$  and thermal fusion was provided on all sides.

(5) Sample 5 (S-5): Aforementioned S-2 placed between two polypropylene non-woven fabric sheets with a metsuke of 50  $\text{g/m}^2$  and thermal fusion was applied to all sides.

(6) Sample 6 (S-6): Commercial "oil removal sheet".

(7) Sample 7 (S-7): Commercial "Paper towel" made of pulp.

(8) Sample 8 (S-8): Polypropylene non-woven fabric with metsuke of 22  $\text{g/m}^2$ .

(9) Sample 9 (S-9): Aforementioned S-6 cut to form strips with a width of 2 mm.

(10) Sample 10 (S-10): Aforementioned S-7 cut to form strips with a width of 2 mm.

(11) Sample 11 (S-11): Aforementioned S-8 cut to form a strips with a width of 2 mm.

[0031] Application examples 1 to 5 and Comparative examples 1 to 3

1 mm of paraffin oil with a viscosity of 45 cps was applied to a glass sheet from a syringe, and the aforementioned samples 1 through 8 were applied with a light pressure and an evaluation was made of the oil absorption. And the results obtained are shown in Table I below.

[0032]

Table I

	Ap Ex 1	Ap Ex 2	Ap Ex 3	Ap Ex 4	Ap Ex 5	Cp Ex 1	Cp Ex 2	Cp Ex 3
Sample	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8
Absorption <sup>(1)</sup>	.DC.	.DC.	.DC.	.C.	.C.	X	X	X

Translator's note: Ap Ex = Application Example

Cp Ex = Comparative Example

Absorption<sup>(1)</sup>: .DC. [double circle] indicates the case where the sample becomes instantly transparent upon absorption of oil and oil residue is absent on the glass sheet and surface of the sample and the oil is completely absorbed by the sample. .C. [circle] indicates that some of the oil is removed from the glass sheet, but a slight residue is detected on the surface of the sample. "X" indicates the case where an oily residue is observed on the glass sheet and high adsorption of oil is observed on the surface of the sample as well.

[0033] Application examples 6 to 8 and Comparative examples 4 to 6

A fine dispersion was formed for equivalent amounts of water and the aforementioned paraffin oil using a homogenizer, and 1 ml of the dispersion produced was applied dropwise to a glass sheet, and the above-mentioned samples 1 through 3 and 6 through 8 were applied with a light pressure and an evaluation was made of the oil absorption. And the results obtained are shown in Table II below.

[0034]

Table II

	Ap Ex 6	Ap Ex 7	Ap Ex 8	Cp Ex 4	Cp Ex 5	Cp Ex 6
Sample	S-1	S-2	S-3	S-6	S-7	S-8
Absorption <sup>(2)</sup>	.DC.	.DC.	.DC.	X	X	X

Translator's note: Ap Ex = Application Example

Cp Ex = Comparative Example

Absorption<sup>(2)</sup> .DC. [double circle] indicates the case where the sample becomes transparent instantly upon absorption of oil and fine droplets of water are observed on the surface of the sample as well as on the glass sheet and oil is selectively absorbed. "X" indicates the case where dispersion of a water and oil residue is observed on the surface of the sample as well as on the glass sheet and selective absorption of oil is absent.

[0035] Application example 9 and Comparative examples 7 to 9

10 g each of sample 2 and samples 9 through 11 were place in a cylindrical stainless steel porous container as shown in Fig. 1, a stainless steel pipe having a screen at the insertion end was placed at the center, and 100 g of a dispersion comprising 90 g of water and 10 g of the aforementioned oil was poured from the upper end of the pipe. The liquid seeped out of the aforementioned cylindrical stainless steel mesh container was collected and the water was evaporated using an evaporator and the amount of residue was measured. And the results obtained are shown in Table III below.

[0036]

Table III

	Ap Ex 1	Ap Ex 2	Cp Ex 8	Cp Ex 9
Sample	S-2	S-9	S-10	S-11
Residue	10 mg <sup>(1)</sup>	5.4 g	3.7 g	1.2 g

Translator's note: Ap Ex = Application Example

Cp Ex = Comparative Example

Furthermore, cleaning of each sample (S-2) after the test with a high proportion of hexane and drying, the test was repeated, the same good results were obtained.

[0037] As is clearly shown in the Table I and Table II above, the selective oil absorber of the present invention is capable of absorbing and retaining large quantities of oil instantly, and it is capable of selectively absorbing oily components from an oil/water mixture. Furthermore, as shown in Table III, the oil separator of the present invention is capable of essentially completely removing oily components from an oil/water mixture.

[0038]

[Effect of the invention] As explained in detail, the selective oil absorber of the present invention is capable of selectively absorbing and retaining large quantities of fats and oils or oil components found on a solid surface, and selectively absorbing oily components in an oil/water mixture almost instantaneously.

Furthermore, the oil separator of the present invention is capable of effectively separating oil components from an oil/water mixture. The present invention can be used in a variety of fields, and the selective oil absorber can be used effectively as oil absorbing sheet, oil cleaning product, etc. Furthermore, the oil separator can be used for purification of waste water containing oily



components.

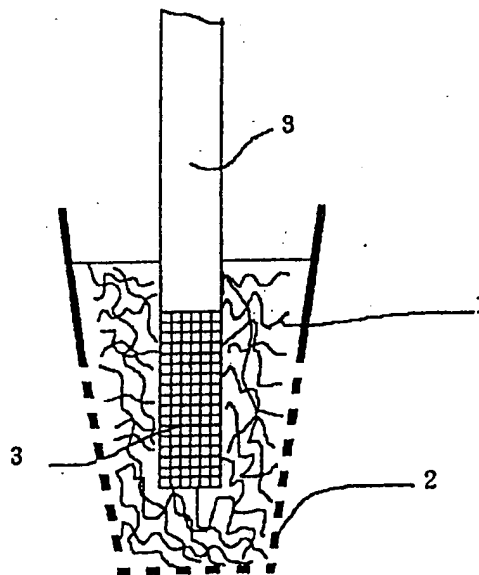
[Brief description of the figure]

[Fig. 1] Side view of an application example of the oil separator of the present invention.

[Explanation of codes]

- 1. Selective oil absorber
- 2. Porous container
- 3. Feed pipe
- 3'. Screened portion of feed pipe

[Fig. 1]



KOKAI PATENT APPLICATION NO. SHO 60-257221

**POROUS FILM WITH HIGH FLEXIBILITY**

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